Cyanogen Ethylation of Methyl- and Ethyl Dichlorosilanes

62-12-13/20

ASSOCIATION: Institute for Organic Chemistry AN USSR imeni N.D.Zelinskiy

(Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk

ŠSSR).

SUBMITTED: July 5, 1957

AVAILABLE: Library of Congress

1. Alkyl-dichlorsilylpropionnitryles-Titration 2. **3** -methyl-dichlorosilylpropionnitryles-Structure-Pyradine catalyst Card 2/2

CIA-RDP86-00513R001859210018-6" APPROVED FOR RELEASE: 08/31/2001

V DOVIN, V M
Petrov, A. D., and Vdovin, V. M.

448

AUTHORS:

TITLE:

Synthesis of 1,1-Diphenyl-4 (or 4,4-)-Alkyl (or Aryl)-Alkanes from 3,3-Diphenyl-butyronitrile (Sintez 1,1-difenil-4 (ili 4,4)alkil (ili aril)-alkanov cherez 3,3-difenilbutironitril)

PERIODICAL:

Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 1, pp. 45-48 (U.S.S.R.)

ABSTRACT:

Referring to the A. D. Grebenyuk and I. P. Tsukervanik report (2) in which the Friedel/Crafts reaction was applied to betachloropropionenitrile, chlorobenzene and even benzene the authors condensed beta-trichloromethylpropionenitrile with benzene according to equation ClC6H5 + ClCH2CH2CN AlCl2 ClC6H4CH2CH2CN and obtained 3,3-diphenylbutyronitrile - a suitable raw material for the synthesis of homologous acid and different ketones - intermediate products of hydrocarbon synthesis. Efforts were also made to introduce certain Grignard reagents into the reaction with Cl_3CCH_2CH_2CN but the reaction was not as anticipated and the condensation products obtained were not soluble in ether. A method of obtaining asymmetric alkyl/aryl hydrocarbons of the 1,1-diphenyl-4(or4,4)alkyl(or aryl)-alkanes from 3,3-diphenylbutyronitrile, is described.

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Synthesis of 1,1-Diphenyl-4 (or 4,4)-Alkyl(or Aryl)-Alkanes from 3,3-Diphenyl butyronitrile

There are 4 references, of which l is Slavic

Academy of Sciences USSR, Institute of Organic Chemistry ASSOCIATION:

(Institut Organicheskoy Khimii, Akademii Nauk SSSR)

PRESENTED BY:

January 9, 1956 SUBMITTED:

AVAILABLE:

Card 2/2

 $\sqrt{4}$

5(3) AUTHORS:

Petrov, A. D., Vdovin, V. M.

SOV/62-58-11-15/26

TITLE:

Synthesis and Properties of Cyanoisopropoxy Silanes and Cyanoisopropoxy Chloro Silanes - Communication 2.

(Sintez i svoystva C-tsianizopropoksisilanov i C-tsianizopropoksikhlorsilanov - Soobshcheniye 2.)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1958, Nr 11, pp 1366-1371 (USSR)

ABSTRACT:

In the present paper the authors studied the following problems: 1) Effect of the structure of alkyl-(aryl)-chloro silanes on the yield of their mono-, di-, and tri-d-cyanoisopropoxy derivatives with a lack of acetone cyanohydrin at room temperature. 2) The behaviour of various oyanoisopropoxy silanes towards hydrolyzing agents in the presence and absence of pyridine. 3) The behaviour of dialkyl-d-cyanoisopropoxy chloro silanes towards the Grignard (Grin'yar) reagent. In this connection the synthesis of 13 different d-cyanoisopropoxy silanes was carried out for the first time. It was demonstrated that in the case of a lacking of acetone cyanohydrin the character of the radicals linked with silicon determines the number of the

card 1/3

Synthesis and Properties of of Cyanoisopropoxy Silanes and of Cyanoisopropoxy Chloro Silanes - Communication 2.

SOV/62-58-11-15/26

can be obtained. In the case of compounds of the type $R_m Si\left[OC(CH_3)_2CN\right]_n$, where n = 1,2,3 and m + n = 4, a considerable stability to hydrolysis was observed. There are 2 figures, 3 tables, and 4 references, 1 of which is Soviet.

ASSOCIATION:

Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D.

Card 2/3

Zelinskiy of the Academy of Sciences, USSR)

CIA-RDP86-00513R001859210018-6 "APPROVED FOR RELEASE: 08/31/2001

. Vdovin, V. M., Petrov, A. D. AUTHORS:

SOY/79-28-10-46/60

THE PROPERTY OF THE PROPERTY O

TITLE:

Synthesis of the Alkenyl-a-CH-Isopropoxy Silanes (Sintez

alkenil-α-CN-izopropoksisilanov)

PERIODICAL:

Zhurnal obshchey khimii, 1958, Vol 28, Nr 10,

pp 2842 - 2845 (USSR)

ABSTRACT:

The interest in these silanes (Refs 1-3) is explained by the easy introduction of the CN-containing radical

into the molecule of the organosilicon compound. Besides, they are stable with regard to a hydrolysis

of the Si-O bond (Refs 2,3). In the paper under discussion, the authors report on the synthesis of the $\alpha\text{-CN-iso-}$ propoxy silanes which contain unsaturated radicals and which are also to be employed in the synthesis of the organosilicon polymers containing the CM-group. Most important in this connexion were the alkenyl-a-CN-isopropoxy silanes and the alkenyl- α -CN-isopropoxyhydride silanes (Refs 4,5,6). The alkenyl-chloro silanes

and alkenyl-hydride-chloro silanes used as initial products, were prepared according to references 7,8,9. In a reaction with cyanohydrin acetone, these chloro

Card 1/3

Synthesis of the Alkenyl-a-CN-Isopropoxy Silanes

SOV/79-26-10-46/60

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silenes were converted into the corresponding α -CN-isopropoxy silene derivatives (Reaction Scheme 1). Contrary to expectations, alkenyltri- α -CN-isopropoxy silenes were obtained, in addition to the expected alkenyldi- α -CN-isopropoxy-hydride silenes, in the reaction of the allyl- and methallyl-dichlere silenes with cyanohydrin acctone and pyridine. In the control test, the reaction of

 $\begin{array}{c} \operatorname{CH}_2 = \operatorname{G---CH}_2 - \operatorname{SiH} \left[\operatorname{OC} \left(\operatorname{CH}_3\right)_2 \operatorname{CN}\right]_2 & \text{with} \\ \operatorname{CH}_3 & \end{array}$

acetonecyanohydrin and pyridine also yielded $CH_2 = C - CH_2 - Si \left[OC(CH_3)_2 CN \right]_3$. Also, $CH_3 Si \left[OC(CH_3)_2 CN \right]_3$

was obtained from $\text{CH}_3\text{SiCl}_2\text{H}$, in accordance with scheme 2. For the attempts to introduce the allyloxy radical into the molecule of the alkyl- α -CN-isopropoxy-chloro silanes, and their results, vide schemes 3 and 4. There are 1 table and 10 references, 6 of which are Soviet.

Card 2/3

Synthesis of the Alkenyl- α -CN-Iso_ropoxy Silanes

SOV/79-28-10-46/60

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR (Institute of Organic Chemistry of the Academy of Sciences, USSR)

SUBMITTED:

July 8, 1957

Card 3/3

CIA-RDP86-00513R001859210018-6" APPROVED FOR RELEASE: 08/31/2001

5(3) AUTHORS:

Petrov, A. D., Vdovin, V. M.

507/62-59-5-33/40

TITLE:

On the Interaction Between Symmetric Tetraalkyldisiloxanes With Dialkyl-dialkenylsilanes and Symmetric Tetraalkyl-dialkenyldisiloxanes (O vzaimodeystvii simmetrichnykh tetraalkildisiloksanov s dialkildialkenilsilanami i simmetrichnymi

tetraalkildialkenildisiloksanami)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1959, Nr 5, pp 939-941 (USSR)

ABSTRACT:

In earlier papers (Refs 1-3) it had been shown that under the action of platinized carbon and heating for several hours in dialkylsilanes an intermolecular hydrogen- and alkenyl condensation takes place. Biradical formed hereby results in a polymer with silicon atoms in the basic chain. This kind of polymerization is based upon the specific effect of platinum catalysts. In this connection the intermolecular condensation reaction of the compounds mentioned in the title was investigated under the influence of the catalyst H₂PtCl₆. It was found

that both reactions developed very easily and within a few minutes. They were highly endothermic and polymers were formed

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with different ratios of silicon hydrocarbon bridges and

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sov/62-59-5-3**3**/40

On the Interaction Between Symmetric Tetraalkyldisiloxanes With Dialkyldialkenylsilanes and Symmetric Tetraalkyldialkenyldisiloxanes

siloxane groupings. Polymeric disiloxanes and polymeric tetrasiloxanes were obtained. The alternating bonds Si-C and Si-O are in the basic chain. The new polymers are thick liquids and have a molecular weight of 800-900 and a viscosity curve that is slightly sloped in dependence on temperature. The carrying out of polymer synthesis is described in the experimental part. The reactions are represented by the equations (2) and (3). There are 1 table and 7 references, 5 of which are Soviet.

ASSOCIATION:

Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED:

October 28, 1958

Card 2/2

5(3) AUTHORS:

Petrov, A.D., Vdovin, V. M.

SOV/62-59-6-35/36

TITLE:

The Synthesis of Polymers With Alternating Siloxane- and Hydrocarbon Links (Sintez polimerov s cheredujushchimisya

siloksanovyni i uglevodorodnyni zven'yani)

PERIODICAL:

Izvestiya Ikademii nauk SSSR. Otdeleniye khimicheskikh nauk,

1959, Nr 6, pp 1139 - 1142 (USSR)

ABSTRACT:

In their investigations the authors found a simple way of synthesizing hydride-organosilicon polymers. These substances were either highmolecular liquids or solid rubber-like substances. The method is based upon the hydrolysis of dichlorosilane in which hydrocarbon-, silicon hydrocarbon-, or siloxane-hydrocarbon chains in desired arrangement between silicon atoms at the end of the chain occur. The equations for the production of dichlorosilane are given. The reactions took place in isopropylalcohol in the presence of the catalyst H₂PtCl₆. The properties of the dichlorosilanes

synthesized are shown in a table. In the experimental part the synthesis itself is described in detail. By means of the hydrolysis of the dichlorosilane with an inner siloxane hydrocarbon chain a glycerin-like grease was obtained. It has a molecular weight of

Card 1/3

The Synthesis of Polymers With Alternating Siloxane- and SOV/62-59-6-35/36 Hydrocarbon Links

3550 and a viscosity whose temperature dependence curve is represented by a figure. It has chain members of the following arrangement: (siloxane hydrocarbon members)

The following polymers with silicon hydrocarbon members

and the following polymers with hydrocarbon members:

Card 2/3

There are 1 figure, 1 table, and 5 references, 4 of which are Soviet.

The Synthesis of Polymers With Alternating Skloxane- and SOV/62-59-6-35/36 Hydrocarbon Links

ASSOCIATION:

Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk

SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of

the Academy of Sciences, USSR)

SUBMITTED:

December 29, 1958

Card 3/3

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77097 SOV/62-59-12-41/43

AUTHORS:

Polyakova, A. M., Suchkova, M. D., Vdovin, V. M., Mironov, V. F., Korshak, V. V., Petrov, A. D.

TITLE:

Concerning the Interaction of Acetylene With Siloxanes

and Silanes. Brief Communications

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh

nauk, 1959, Nr 12, pp 2257-2259 (USSR)

ABSTRACT:

Purified acetylene in reaction with disiloxanes

 $\mathrm{HR}_2\mathrm{SiOSiR}_2\mathrm{H}$ (where R = CH₃ and C₂H₅) under atmospheric

pressure, in presence of chloroplatinic acid in isopropanol or platinum on carbon, gave polymers in the form of thick oils. IR spectra and other analytical data indicate that the macromolecules of these poly-

mers consist of units:

$$-\begin{bmatrix} R & R & R \\ -Si - O - Si - CH_2 - CH_2 - \end{bmatrix}_{n}^{-1}$$

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Concerning the Interaction of Acetylene With Siloxanes and Silanes. Brief Communications

77097 SOV/62-59-12-41/43

where n = 2 to 14. Physical and chemical constants of polymers obtained in 30.0 to 87.4% yield from tetramethyl-, dimethyldiethyl-, and tetraethyldisiloxanes are tabulated. In similar reactions, purified acetylene with methylphenylchlorosilane $(CH_3)C_6H_5SiClH$ under atmospheric pressure, in the presence of chloroplatinic acid in isopropanol, gave 1,2-bis-(phenylmethylchlorosilyl)ethane Cl(CH3)(C6H5)SiCH2CH2Si(C6H5) (CH₂)Cl in 88% yield. Reaction of acetylene with methyldichlorosilane CH3SiCl2H gave similarly 1,2-bis-(methyldichlorosilyl)ethane ${\rm Cl}_2({\rm CH}_3){\rm SiCH}_2{\rm CH}_2{\rm Si}({\rm CH}_3){\rm Cl}_2$ in 9% yield; the balance consisted in the unreacted starting silane. Acetylene must be completely free of any impurities which could poison the catalyst. IR spectra were taken by N. A. Chumayevskiy. There is 1 table; and 7 references, 2 U.S., 1 Japanese, 4 Soviet. The U.S. references are: J. W. Curry, J. Amer.

Card 2/3

Concerning the Interaction of Acetylene With Siloxanes and Silanes. Brief

77097 sov/62-59-12-41/43

Communications

Chem. Soc., 78, 1636 (1956); J. L. Speier, D. B. Hook, U.S. Pat. 2823218, 11-02-58.

Institute of Elemento-Organic Compounds, Academy of ASSOCIATION:

Sciences, USSR, and N. D. Zelinskiy Institute of

Organic Chemistry, Academy of Sciences, USSR (Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR i Institut organicheskoy khimii imeni N. D. Zelinskogo

Akademii nauk SSSR)

SUBMITTED:

May 25, 1959

Card 3/3

5(3) sov/79-29-9-21/76

AUTHORS: Petrov, A. D., Vdovin, V. M.

TITLE: Synthesis and Reactions of β -Cyanoethyl Silanes

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9, pp 2910-2914(USSR)

ABSTRACT: Russian and foreign chemists synthesized β-cyanoethyl silanes

(Refs 2-8) according to the reaction

 $RSiCl_2H+CH_2=CHCN \xrightarrow{\text{catalysts}} RSi(Cl_2)CH_2CH_2CN \qquad (2), \text{ where}$

R=Cl, CH₃, C₂H₅. It was found in this connection that β -cyanoethyl silanes, unlike α -cyanoalkyl silanes (Refs 3, 9-11), react with the cyano group, and therefore may serve as initial products for the synthesis of various carbofunctional organosilicon compounds. A new method of synthesizing β -cyanoethyl silanes, namely the β -cyanoethyl trialkyl silanes, is described in the present paper. It is based on the well-known reaction by R. H. Wagner and Zook (Ref 12) (Scheme 3 and 4). β -cyanoethyl trialkyl silanes were obtained by the authors according

to the scheme

Card 1/3 $R(CH_3)_2 SiCH_2 X + CH_3 CN + Na \longrightarrow R(CH_3)_2 SiCH_2 CH_2 CN + Na X + <math>\frac{1}{2}$ H₂,

501/79-29-9-21/76

Synthesis and Reactions of β -Cyancethyl Silanes

where R=CH3, C2H5; X=Cl or J (5). In the case of chloro methyl trialkyl silanes, NaJ was used as a catalyst. The authors did not succeed in separating the dialkylation products of acetonitrile (Reaction 4). The highest yield of silicon-containing nitrile (52%) was obtained by using iodomethyl trimethyl silane. The structure of β -cyancethyl trimethyl silane resulting after reaction (5), was proven by reaction (6) and (7). Ketone(CH₃)₃SiCH₂CH₂COCH₃, which the authors obtained by re-(6), has been also synthesized, as is known, by action other methods (Refs 2, 14), like, for example, β -cyanoethyl trimethyl silane. (CH3)3SiCH2CN obtained by M. Prober (Ref 10) by reaction of trimethyl chlorosilane with acetonitrile and sodium, could be obtained in a yield of 2% only, because the reaction took place according to another scheme, and yielded $(CH_3)_3$ SiNC and $(CH_3)_3$ Si-N=C=CHSi(CH₃)₃, along with other products. With β-trichloro silyl propionitrile, synthesized also by A. D. Petrov according to scheme (1), it is possible, as shown by reactions (8-10), to obtain also β -cyanoethyl silanes with functional groups on the silicon. There are

Card 2/3

507/79-29-9-21/76

Synthesis and Reactions of β -Cyanoethyl Silanes

20 references, 10 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR

(Institute of Organic Chemistry of the Academy of Sciences, USSR)

July 28, 1958 SUBMITTED:

Card 3/3

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AUTHORS:

Petrov, A. D., Corresponding Member

SOV/20-128-6-30/63

AS USSR, Vdovin, V. M., Sultanov, R.

TITLE:

Synthesis of α,ω-Di-(cyano-alkyl) Tetraalkyl Disiloxanes

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 6, pp 1204 - 1207

(USSR)

ABSTRACT:

On the basis of analogy with organic dinitriles, it is to be expected that also organo-silicon compounds having 2 fragments [A] in the molecule $(A = \Xi Si(CH_2)_n CN$, where $n \ge 2)$ may be used as

initial raw materials for the production of α,ω -diffunctional compounds utilizable for the synthesis of organo-silicon polymers. The present paper refers to the synthesis of α,ω -dinitriles of type [B] (see Diagram). The addition of 2 moles of allyl cyanide to $HR_2SiOSiR_2H$ by means of I. L. Speir's (Ref 7) catalyst (Ta-

ble 1, Experiments Nr 5 and 6) was not successful. Ethyl-methyl chlorosilane has already been added to cyanous olefines (Table 1, Experiments 3,7). The synthesis of the desired α,ω -dinitriles was possible by hydrolysis of the monochlorides obtained. Water was used as a hydrolyzing agent. By use of concentrated HCl and under harder conditions, the corresponding α,ω -acid was formed.

Card 1/2

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Synthesis of α,ω -Di-(cyano-alkyl) Tetraalkyl Disiloxanes SOY/20-128-6-30/63

Besides, the authors used the available \gamma-cyano-propyl-alkyl dichlorosilanes for the said purpose (Table 2. Experiments 1 and 2). Here, the circumstance was made use of that the compound -SiCl, with respect to Grignard's reagent, is more reactive than -C ≡N (Refs 1,2) (Diagram). On the basis of a similar reaction, (NCCH2CH2Si(C2H5)2)20 was also obtained from Cl3SiCH2CH2CH and ethyl-magnesium chloride. The former initial substance can be easily produced at present (see Diagram, as well as Patent Ref 5, further Ref 6). The authors carried out the addition of cyanous olefines to hydrosilanes by boiling the reaction mixture in a glass flask with recooler according to reference 7 in the presence of 0.1 n-solution of H_PtCl in isopropyl alcohol. Table 1 shows the results, table 2 the properties of the nitriles

and dinitriles obtained. There are 2 tables and 9 references, 4 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED:

June 27, 1959

Card 2/2

APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001859210018-6"

x	And the There foreign ton of 3111con-containing fairties and the There foreing Properties of Polygaide Abtained From the Amine Produced Thereby Oblaide Abtained Andrew Produced Thereby 1910 Andrew Andrew Land State 1939, Tol 129, Kr 5, pp 1064 - 1067 (1922)		A	and amonia. The anies fractive we stated to intilled and and amonia. The anies fractive was readily distilled by fractionaling the acts yields. Its degree of purity sees of readily distilled by fractionaling and states. Table is a specifies the experiental conditions and yields. Table 5 supplies the constants of animes and their distributes. In this animer the following symmetrical did-animo-buryl. Stran-layed distinctions were produced in [6 mes Schere] along with its sail with reciphiant its acts at a the treaphants and their series the condition of the law shared and is in 1 3.54. III [8 mes Schere in the respinishing of the soil of the law share and at in 1 3.54. III - 106. Table 2 stress the constants of the sails with the present the constants of the law and their sails with terepibalic acid. The yield of the constants of the sails with terepibalic acid. The yield of the constants of the law and their asing with terepibalic acid. The yield of the collect the polymandes were obtained by soluble in 50% allowed. The polymandes were obtained by	heating (polycondenation) of the produced salts in mitted. gen exhaphers. They are pale-yellow, horry, electic, tenne- parent resins of sarophous tructure, sell estable in orsel and consented E550, They seell is byleoblate and furnin sold, but do not salve, Table 3 shows the condi- tions of polycondenation. All these polysaides, when salted, yield fibrus, abloh are dilatable by 500-405% at low temper- ature, the stability of the fibra is no over high. The re- salts obtained confirmed that the substitution of salve) redicals on the sillons acce by tabl redicals occurs the pelgemide salting temperature to drop, the silonane group in the principal chaim increases the flexibility and elections, of which are Societ.	ASSOCIATION: Institut organichestoy thisil is. N. D. Zelinkvogo akadesii auk 533M (Institute of Organic Chanitati Jison, N. D. Ellin. ky of the Acadesy of Batences, ESSB Taesovany nucleus instalcionatellati institute of Spatesii (1): Jack 4/5 Union Scientific Research Institute of Spatesiic Resea.
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78087 SOV/62-60-1-33/37

AUTHORS:

Petrov, A. D., Vdovin, V. M., Pushenevaya, K. S.

TITLE:

Brief Communications. Concerning Reaction of α , ω -DI(chloroalkyl)tetraalkyldisiloxanes With

Ethylamine

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh

nauk, 1960, Nr 1, pp 143-145 (USSR)

ABSTRACT:

In order to obtain organosilicon diamines of the type:

 $H-N(CH_2)_n-\dot{S}i-O-\dot{S}i(CH_2)_nN-H$,

where n = 1, 3, the reaction of ethylamine with sym-di-(chloromethyl) tetramethyldisiloxane and $sym-di(\gamma-chloro-propyl)$ tetraalkyldisiloxane was studied. The sym-

di(chloromethyl)tetramethyldisiloxane reacts with

Card 1/5

ethylamine at room temperature; however, the reaction proceeds in an unexpected direction (see scheme) with

Brief Communications. Concerning Reaction of 78087 C., ω -Di(chloroalkyl)tetraalkyldisiloxanes With SOV/62-50-1-33/37 Ethylamine

the formation of cyclic monoamine in about 90% yield.

The sym-di(γ -chloropropyl)tetraalkyldisiloxane does not react with ethylamine at room temperature even on standing for 10 days; but it reacts with ethylamine at 100° in autoclaves, according to the usual scheme for this type of reaction:

[CICH2CH2CH2Si (CH2) (C2H3)]20 + 4C2H3NH2 --

 $\rightarrow [(C_2N_4)NHCH_2CH_2CH_2Si~(CH_3)(C_2H_4)]_2O + 2C_2H_4\cdot NH_2\cdot HCI$

The compounds obtained and their properties are shown in Table 1. There are 1 table; and 7 references, 2 U.S., 5 Soviet. The 2 U.S. references are: P. D. George, I. R. Elliott, J. Amer. Chem. Soc., 77, 3493 (1955); J. E.

Card 2/5

Tarlet Communications. Concerning Reaction of 7808/ C., CJ-DI(chloroalkyl)tetraalkyldicilosanen With 807/62-60-1-33/37 Ethylamine

Table 1. Properties of Compounds Obtained. (a) Compound Nr; (b) formula; (c) yield (%); (d) bp in °C (p in mm of Hg); (e) found MR; (f) MR, calculated; (g) elemental analysis in %; (h) found; (i) calculated; (*) for literature data see: A. D. Petrov, V. A. Ponomarenko, and others, Izv. AN SSSR. Otd. knim. n. 1206 (1957); (**) based on chloride taken.

Card 3/5

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•		C	D	"D	d_4^{20}	E	F	G	
1*	[CICH ₂ CH ₂ CH ₃]Si(CH ₄)(C ₄ H ₄)Cl	35	401 409 945	<u> </u>	<u> </u> 	<u> </u>		<u> </u>	
11^	[CICH_CH_CH_ISI(C_H_),CI		101—103(34)	1,4553	0,8815	1	:	·	;
111	ļ	44	91-93(10)	1,4600	1,0400		1	Cl 35,6; 35,8	CI 35,
	[(CICH, CH, CH,)SI(C, H,)(CH,)],O	70	125(3)	1,4577	0,9950	86,4	86,3	Si 18,1	i
IV ((CICH)	{(ClCH ₂ CH ₄ CH ₄)Si(C ₄ H ₄) ₄] ₂ O	61	165168(2)	1,4654	1,0062	91,7	95,2	-	Si 17,
v	ln(c¹n¹)ucn¹cn²cn²cn'k(cn')(c¹n')l³0	69**	152(2)	1,4511	0,8745	102,5	102,5	Si 17.0; 16.6 C 48.9; 48.7 H 9.2 Si 16.1; 16.5	Si 16, C 48,9 H 9,4 Si 16,8
. 1	(CII')'-2!-CII'	91,5**	61(17)	1,4320	0,8768	60,1	59,9	C 58.2; 58,1 H 12.5; 12.1 N 8,8; 8,7 C 46.5; 46,3 H 10.4; 10.5	C 57,8 H 12,1 N 84 C 47,2 H 10,4 N 7,5
- 1	[H(C₂H₃)NCH₂CH₂Si(CH₃)₂]₂O	58**	123-126(2)	1,4440	0,8658	93,4	93,5	N 9,2; 9,2	
/111 [[]	[HCH3NCH3CH3CH3Si(CH3)3]3O	53**	112114(2)	1,4433	0,8733	81,0	81,2	N 9,9; 10,0	N 9,1 N 11,1

Card 4/5

Brief Communications. Concerning Reaction of 78087 α , ω -Di(chloroalkyl)tetraalkyldisiloxanes With SOV/62-60-1-33/37 Ethylamine

Noll, I. L. Speir, B. F. daubert, J. Amer. Chem. Soc., 73, 3867 (1951).

73, 3007 (1951)

ASSOCIATION: N. D. Zelinskiy Institute of Organic Chemistry, Academy of Science USSR (Institut organicheskoy

khimii imeni N. D. Zelinskogo Akademii nauk SSSR)

SUBMITTED: June 27, 1959

Card 5/5

VDOVIN, V.M.

5.3700C also 2109, 2209

831477 \$/190/60/002/009/008/019 B004/B060

AUTHORS:

Polyakova, A. M., Korshak, V. V., Suchkova, M. D.,

Vdovin, V. M., Chumayevskiy, N. A.

TITLE:

Production and Structure Investigation of Polymers Containing Siloxane- and Hydrocarbon Links in the Principal Chain

of Macromolecules. IV.

PERIODICAL:

Vysokomolekulyarnyye soyedineniya, 1960, Vol. 2, No. 9,

pp. 1360-1369

TEXT: The authors had previously studied (Refs. 1-3) the reaction of acetylene with dihydro tetraalkyl disiloxanes, and determined the structure of the polymers obtained on the strength of their infrared spectrum. In the present article, the authors report on the reaction of acetylene with dihydro siloxanes of varying molar ratios of the reagents. The reaction yields chain-like polymers with different terminal groups. The infrared spectra were examined for the absorption bands of the stretching vibrations of the -Si-H terminal group (2100-2150 cm⁻¹), of the C=C bond (vinyl group 1595-1600 cm⁻¹, allyl group 1625-1635 cm⁻¹), and the Card 1/4

APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001859210018-6"

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Production and Structure Investigation of S/190/60/002/009/008/019 Polymers Containing Siloxane- and Hydrocarbon B004/B060 Links in the Principal Chain of Macromolecules. IV

asymmetric stretching vibrations of the =CH₂ terminal group (3050 cm⁻¹). The spectra shown in Fig. 1 reveal that the reaction of acetylene with excess dihydro siloxane yields a polymerization product (I) having -Si-H terminal groups. In the case of an acetylene excess, however, polymer (II) forms with -CH=CH, as terminal groups. This could also be proven chemically. The oily polymerizate (II) was heated to 130° C at 6000 atm and at atmospheric pressure with tert-butyl peroxide. The product obtained was insoluble in all solvents. If (II) is caused to react with tetraalkyl dihydro disiloxane in the presence of H2PtCl6.6H2O, the chain is prolonged, and the resulting new polymerizate has -\$i-H terminal groups. Similar reactions were carried out with acetylene and the polymers (III) described in Ref. 2 (with -SigH as terminal group), and (IV)(with -CH=CH2 as terminal group). The reaction of (III) with acetylene yielded a polymerization product with -CH=CH, as terminal group; the reaction of (IV) with tetraethyl dihydro disiloxane yielded a polymerizate with -\$i-H as terminal Card 2/A

83477

Production and Structure Investigation of Poly- S/190/60/002/009;008/019 mers Containing Siloxane- and Hydrocarbon Links B004/B060 in the Principal Chain of Macromolecules. IV

group (infrared spectra Fig. 2). In both cases, the molecular weight increased, and the chain grew longer. Furthermore, dimethyl diphenyl dihydro disiloxane was caused to react with acetylene. The polymerizate, a viscous mass, had the molecular weight 1670. Table 1 shows the results of the reaction of acetylene with tetramethyl— and dimethyl diethyl dihydro disiloxane at a pressure of 15 atm. The infrared spectra (Fig. 3) of the oily products revealed both the presence of C=C bonds and of =CH2 as terminal groups. Analyses and molecular weights of the fractions distilled in vacuum are given in Table 2. Only addition products and dimers were obtained on the reaction of phenyl acetylene and diphenyl acetylene with dihydro siloxanes (Table 3). With the exception of the reaction product from diphenyl acetylene and tetraethyl dihydro disiloxane, whose structure is still unclear, the infrared spectra (Fig. 4) revealed -Si-H bands. The infrared spectra were taken with a BNKC M-3 (VIKS M-3) spectrophotometer. The authors thank A. D. Petrov and I. V. Obreimov for interest displayed in the work. There are 4 figures, 3 tables, and 6 references: 4 Soviet, 1 US, and 1 German.

Card 3/4

Production and Structure Investigation of Poly- S/190/60/002/009/008/019 mers Containing Siloxane- and Hydrocarbon Links B004/B060 in the Principal Chain of Macromolecules. IV .

ASSOCIATION:

Institut elementoorganicheskikh soyedineniy AN SSSR (Institute of Elemental-organic Compounds of the AS USSR). Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the AS USSR)

SUBMITTED:

April 4, 1960

V

Card 4/4

5.3700B

S/062/60/000/03/07/007 B008/B006

AUTHORS:

Petrov, A. D., Vdovin, V. M.

TITLE:

On Catalytic Disproportionation of Alkyl (Alkenyl)

Dichloro Silanes

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh

nauk, 1960, No. 3, pp. 519-526

TEXT: The disproportionation of alkyl (and alkenyl) dichloro silanes using pyridine or Adipodinitrile as catalysts was investigated. The reaction, which always proceeds according to Scheme (1)

2 RSiCl₂H --> RSiClH₂ + RSiCl₃, can be used for preparing alkyl (alkenyl) monochloro silanes. Yields of RSiClH₂ compounds obtained in the presence of the above-mentioned catalysts and from varying amounts of RSiCl₂H are shown in Table 1 and Figs. 1-6. The properties of the alkyl (alkenyl) chloro milanes synthesized for the first time are listed in Table 2. Pyridine, which has not been described as a catalyst for disproportionation in publications, resembles Adipodinitrile in its

Card 1/3

On Catalytic Disproportionation of Alkyl (Alkenyl) Dichloro Silanes

S/062/60/000/03/07/007 B008/B006

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catalytic activity with respect to allyl dichlorosilanes, and was even more efficient than the latter catalyst in the disproportionation of ethyl dichloro silane. To increase the reaction rate larger amounts of catalysts are required. Contrary to all other tests, experiments with CH2 = CHCH2SiCl2H gave slightly lower yields of allyl trichloro silane than allyl chloro silane. Yields of RSiClH2 and RSiCl3 amounted to 70 - 99% of the initial RSiCl2H. Different results were only obtained in the experiments No. 1, 11, and 7. In studying the reaction (1), it was found that the structure of the organic radical in RSiCl2H has a marked effect on the reaction rate. It can be seen in Table 1 that as the radical becomes smaller down to the ethyl radical, the reaction rate decreases and finally, in the case of R = CH3, the reaction does not occur at all. The dependence of the reaction rate on the type of radical bonded with silicon is specially pronounced in the case of alkenyl radicals with a short bond in the γ position with respect to silicon. The authors thank L. A. Leytes for taking and analyzing the spectra. The following persons are mentioned: B. N. Dolgov, M. G. Voronko♥, S. N. Borisov, V. F. Mironov, and G. I. Nikishin. There are

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Card 2/3

On Catalytic Disproportionation of Alkyl

S/062/60/000/03/07/007 B008/B006

(Alkenyl) Dichloro Silanes

6 figures, 2 tables, and 19 references, 12 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D.

Zelinskiy of the Academy of Sciences USSR)

SUBMITTED:

July 28, 1958, supplemented on July 4, 1959

card 3/3

2209,1273,1274

s/062/60/000/010/014/018 B015/B064

5 3700

AUTHORS:

Freydlin, L. Kh., Petrov, A. D., Sladkova, T. A., and

Vdovin. V. M.

TITLE:

Catalytic Hydrogenation of Silicon Containing β - and

y-Nitriles o

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh

nauk, 1960, No. 10, pp. 1878 - 1881

TEXT: A hydrogenation of the β -cyanoethyl- and γ -cyanopropyl silanes to the corresponding primary amines was carried out on metal catalysts. The hydrogenation was made in a rotating steel autoclave (volume 0.1751) by a method already described. The effect of the composition of the catalyst, the reaction conditions, and the molecular structure of the cyanoalkyl silanes upon the amine yield was investigated. First, the hydrogenation of cyanoalkyl silanes without alkoxyl groups was studied, and then with two or three alkoxyl groups on the silicon atom (Table 1, experimental conditions and results). Just as in the hydrogenation of

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Catalytic Hydrogenation of Silicon Containing β - and γ -Nitriles

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aliphatic nitriles containing no silicon atoms, hydrogenation of silicon containing nitriles on cobalt skeleton catalysts was found to be most selective. Hydrogenation of β -cyanoethyl trialkoxy silanes can be carried out only in the presence of ammonia. In the presence of ammonia, primary amines are preferably formed. The properties of the silicon containing primary amines thus produced are given in Table 2. There are 2 tables and 8 references: 4 Soviet, 1 German, 2 US, and 1 Japanese.

ASSOCIATION: In

Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry

imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED:

March 9, 1960

Card 2/2

"APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001859210018-6

5.3600

78267 **sov/**79**-30-3-21/**69

AUTHORS:

Vdovin, V. M., Fetrov, A. D.

TITLE:

Synthesis and Properties of α , ω -Polychlorodisily1-

alkanes

PERIODICAL:

Zhurnal obshchey khimii, 1960, Vol 30, Nr 3,

pp 838-845 (USSR)

ABSTRACT:

The work at hand was devoted to the study of the order of addition of silanes to vinyl- and allyl-containing organosilicon compounds in the presence of H_2PtCl_6, and to the use of this simple method for synthesis of known Cl_, ω -polychlorodisilanes, previously prepared by other methods, as well as of new compounds of Cl_, ω -polychlorodisilanes with di-, tri-, and hexamethylene, organosilicon, and hydrocarbon-siloxane bridges. The order of addition of chloro (or chloroalkyl) silyl group to vinyl-containing organosilicon compounds is shown by the following scheme, where one can assume that the

card 1/7

"APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001859210018-6

Synthesis and Properties of α , $\omega\text{-Polychlorodisilylalkanes}$

78267 80V/79-30-3-21/69

addition of silyl group, in the presence of $\rm H_2PtCl_6$, occurs contrary to Markownikoff's rule, in the manner of schemes 5-9.

Scheme 1-4

Card 2/7

Synthesis and Properties of $oldsymbol{lpha}$, ω -Polychlorodisilyalkanes

(5)
$$\rightarrow$$
SiCH=CH₂+HSi \leftarrow \rightarrow SiCH₂CH₂Si \leftarrow

(5)
$$\Rightarrow$$
 SiCH=CH₂ + HSi \leftarrow \rightarrow SiCH₂CH₂Si \leftarrow

R

R

(6) CH₂=CHCH₂SiCH₂CH=CH₂ + 2HSi \leftarrow \rightarrow SiCH₂CH₂CH₂CH₂CH₂CH₂CH₂Si \leftarrow
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card 3/7

Scheme 5-9

"APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001859210018-6

Synthesis and Properties of α , ω -Polychlorodisilylalkanes

78267 sov/79-30-3-21/69

The properties of the prepared compounds are shown in Table 2.

Table 2. Key: (A) Properties of C, C -polychlorodisilanes and their derivatives; (B) Nr; (C) Adducts and their derivatives; (D) Bp (pressure in mm); (E) Found; (F) Calculated; (G) Empirical Formula; (*) Prepared for the first time.

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Polyc	s and Properties of $lpha$, hlorodisilyalkanes	A To	h10 2		MF		9-3-81/0: G
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	· J	mρ 15.2°	1,3714	1.5310	76.1	76,4	$C_9H_9Si_2Cl_5$
	g_{ij}^{2} sign $_{i}^{2}$ gu $_{i}^{2}$ gu $_{i}^{2}$ gu $_{i}^{2}$ gu $_{i}^{2}$ gu $_{i}^{2}$ gu	(1.5					C ₄ H ₁₀ Si ₂ Cl ₄
	cigorysion cursicaty) cla	10911					
	an energy track.*	mp 32.5	1.2232	1.4170	61.7	!	$C_3H_{32}Si_2CI_1$
	օկտիչուկ արությունը և բանական և	(758) 100	0.8039	1.447	76.5	76.5	$C_{12}U_{30}Si_{2}$
5	(chigherin)sicilycilycilysicily)(chigh	(1)		1			
		150.5 151	5 0.752	2 1.419	5		$C_8 H_{12} Si_2$
6	(CII392SICII2CII2SI(CII3)3	(7° 3) 187 691	21		-	-	$C_{10}H_{21}O_{8}Si_{2}$
7	(C1Pcon)*(C1P)sicit*th*sic51P)(oocc1P)*,	$m\rho_3^{34.5}$	·-				11 (1) (3)
	(હ્યાર્થેઇ)ર્મેલાન્ટે)ટાલાર્મેલાર્ચ્યાલહ્યાર્થે,મહાનું)	792-80 (1.5)	0,930	1.41	80 79.	9 80	$0 C_{12}\Pi_{36}O_{1}Si_{2}$
8		, (10)	•	•	(+	able	contid)
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Synthesis	and	Properties	of	α,
(1) -Polych	loro	lisilyalkand	es	

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			20	20	M	₹ø]	G
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	(crl(crP)zicirl.irrzi(crP)(crlr)-pt.	137 - 1382	1,0850	1,465ki	113.2	112.5	C ₁₂ H ₅₀ OSi ₄ Cl ₄
9	суваснуснусныен	110-110.5	İ	1	64.3	61.2	C ₄ H ₉ Si ₂ Cl ₅
11	(લાકુ)ક્કાલાકુલાકુલાકુલ(લાકુ)લાકુ	199200 (742)	1	1,4430	i		C ₇ H ₁₈ Si ₂ Cl ₂ C ₄ H ₂₄ Si ₂
12	(૯ાકુ),ુકાલામૂદામૂદામૂકા(૯ાકુ)	171.7 (747)	1	1 1.422	0 103.7	103.4	$C_{12}H_{28}Si_3Cl_4$
13.	(cP(crP)sicriPcrifcriPFs)(ત્નાપ્રેવ	148—149 (2) 131—132	1	8 1.471	1	1	$C_6\Pi_{12}\mathrm{Si_2Cl_6}$
14	(CP2ICH*CH*CH*)*	(4) 119—121	1.131	0 1.46	50 76.	1 75.4	4 C.H.SigCl
15	[cP(cP)PS(c1Pc1P7)F	(3) 137—139 (2)	1.12	73 1.47	37 84.	į.	5 CtoH22Si2Cl4
16 17	CH=CH2	. 1	0.91	74 1.44	90 94.	5 94.	4 CiaHaiSiaCl

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"APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001859210018-6

Synthesis and Properties of CL, $\widetilde{\omega}$ -Polychlorodisilyalkanes

78267 SOV/79-30-3-21/69

There are 2 tables; 3 figures; and 13 references, 10 Soviet, 2 U.S., 1 Japanese. The 2 U.S. references are: Burkhard, C. A., Krieble, R. U., J. Am. Chem. Soc., 69, 2687 (1947); Speir, I. L., J. Am. Chem. Soc., 79, 977 (1957).

ASSOCIATION:

Institute of Organic Chemistry of the Academy of Sciences of the USSR (Institut organicheskoy

khimii Akademii nauk SSSR)

SUBMITTED:

March 7, 1959

Card 7/7

15.8116 also 1164

S/062/61/000/002/007/012 B115/B207

AUTHORS:

Vdovin, V. M., Pushchevaya, K. S., and Petrov, A. D.

TITLE:

Organosilicon compounds with hydrocarbon bridges between

the silicon atoms. Report no. 1. Interaction of

1,2-disilethanes with metal halides

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh

nauk, no. 2, 1961, 281-286

TEXT: The authors found that the properties of the Si-R-Si group (R = hydrocarbon radical) have hitherto been insufficiently investigated, and therefore devoted this paper to studies of substances containing a

disilethane group \longrightarrow Si-CH₂-CH₂-Si \Longrightarrow with methyl radicals and chlorine

atoms on silicon atoms. They studied the effect of metal halides having the properties of Lewis acids upon the mentioned substances. The metal halides were subdivided into three groups owing to their interaction with 1,2-hexamethyl disilethane: Group I: Halides not reacting with

Card_1/7

S/062/61/000/002/007/012 B115/B207

Organosilicon compounds with ...

hexamethyl disilethane: ZnCl₂, TiCl₄, SnCl₄, BF₃ etherate, FeCl₂. Group II: FeCl 3 reacts with formation of low-molecular compounds: trimethyl chloro silane and, obviously, ethylene. This proves the simultaneous splitting of the Si-C bond and the elimination of the carbon chain (bridge). The decomposition proceeds according to the reaction schemes (1) and (2).

 $CH_3)_3$ SiCH₂CH₂Si (CH₃)₃ + Fe₂Cl₄ \rightarrow (CH₃)₃ SiCl + ClCH₂CH₂Si (CH₃)₂ + 2FeCl₅ (1) CICH₂CH₃Si (CH₃)₃ → CH₃=CH₅+ (CH₃)₃SiCl

Group III: Aluminum halides causing the formation of Si(CH3)4 and silicon-containing polymers. By moderate heating of (CH3)3SiCH2-CH2Si(CH3) with AlX3, 0.7-0.9 M Si(CH3)4 is separated. At the same time, a polymer of the following structure: [-Si(CH3)2-CH2-CH2-] forms in the reaction mixture. Under special conditions (minimum amount of

Card 2/7

89911 S/062/61/000/002/007/012 B115/B207 Organosilicon compounds with ... catalyst and interruption of the reaction at the moment where the precipitate reached ~ 0.3 M Si(CH₃)₄) two compounds were separated from this polymer: $\left[-\text{Si}(\text{CH}_3)_2\text{CH}_2-\text{CH}_2-\right]_n$, where n = 2,3. The reaction may be represented by the following schemes: (3) or (4). $(CH_3)_3\,SICH_3CH_5SI\,(CH_3)_3 + \Lambda l_2X_4 \,\,\rightarrow\,\, (CH_3)_3\,SICH_2CH_5SI\,(CH_3)_3 \,\,\cdot\,\, \Lambda l_2X_4$ $CH_3 \quad \frac{1}{\downarrow} \quad Si \; (CH_3)_2 \; CH_2CH_3 \quad \frac{1}{\downarrow} \quad Si \; (CH_3)_3 \; \cdot \; Al_2X_6 \; \rightarrow \; (SiCH_3)_4 \; + \; Al_2X_6 \; + \;$ + [-Si (CH₃)₂ CH₂CH₃-] (3) $_{n}[-\text{Si} (\text{CH}_{3})_{3} \text{CH}_{2}\text{CH}_{2}-] \rightarrow [-\text{Si} (\text{CH}_{3})_{2} \text{CH}_{2}\text{CH}_{2}-]_{n}$ $(CH_3)_3$ SiCH₂CH₂ $\frac{1}{1}$ Si $(CH_3)_3$ · Al₂X₆ + CH₃ $\frac{1}{1}$ - Si $(CH_3)_3$ CH₂CH₂Si $(CH_3)_3$ \rightarrow → (CH₃)₄Si + Al₂X₆ + (CH₃)₂SiCH₂CH₃Si (CH₃)₃ CH₂CH₂Si (CH₃)₃ (4)card 3/7

Organosilicon compounds with ...

Card 4/7

S/062/61/000/002/007/012 B115/B207

The linear dimer forming in accordance with scheme (4), is transformed in a similar manner into linear polymers of the type: $(CH_3)_3SiCH_2CH_2[Si(CH_3)_2CH_2CH_2]_nSi(CH_3)_3$, or into cyclic polymers of the $\left[-\text{Si}(\text{CH}_3)_2 - \text{CH}_2\text{CH}_2 - \right]_n$ type. The two processes occur with separation of $(\mathrm{CH_2})_A\mathrm{Si}$. Furthermore, the authors studied the effect of the substituents on the silicon atom of 1,2-disilethanes upon the direction of polycondensation. They found that the conversion of compounds with disilethane groups only proceeds if at least one silicon atom is linked with three CH_2 radicals. As regards the activity of the interaction with AlCl3 and AlBr3, the disilethanes studied form the follow- $(\text{CH}_3)_3 \text{sich}_2 \text{CH}_2 \text{Si}(\text{CH}_3)_3 > (\text{CH}_3)_3 \text{sich}_2 \text{CH}_2 \text{Si}(\text{CH}_3) \text{Cl}_2 >$ ing series: $(CH_3)_3$ SiCH₂CH₂SiCl₃ $\gg (CH_3)$ Cl₂SiCH₂CH₂SiCl₂(CH₃), Cl₃SiCH₂CH₂SiCl₃. With disilethanes having only one Si(CH3)3 group and one Si(R)Cl2 group, the conversion proceeds according to schemes (6) and (7) which are similar to (3) and (4),

83977 S/062/61/000/002/007/012 B115/B207 Organosilicon compounds with ... respectively. Cl₂ (R) SICH₂CH₃ $\xrightarrow{1}$ Si (CH₃)₃·Al₂X₄ + Cl $\xrightarrow{1}$ SiCl (R) CH₂CH₂Si (CH₃)₃ \rightarrow \rightarrow (CH₃)₃ SiCH₂CH₂SiCl (R) CH₂CH₃Si (R) Cl₂ + Al₃X₆ + (CH₃)₃ SiCl и т. д. Cl₂ (R) SiCH₂CH₂ $\xrightarrow{1}$ Si (CH₃)₃ · Al₂X₄ + CH₃ $\xrightarrow{1}$ Si (CH₃)₂ CH₂CH₂SiCl₂ (R) \rightarrow → Si (CH₃)₄ + Al₂X₆ + Cl₂ (R) SiCH₂CH₂Si (CH₃)₃ CH₂CH₂Si (R) Cl₂ (7) и т. д., где R=-Cl или --CH₃ The fact that in the interaction of AlX3 with (CH3)3SiCH2CH2SiCl3 the Si(CH3)4 is formed proves that the polycondensation found follows, at least partly, scheme (4). This was also confirmed by the experiment in which the authors caused 10 mole% AlBr3 to act upon the equimolar mixture of (CH₃)₃SiCH₂-CH₂Si(CH₃)₃ and Cl₂(CH₃)SiCH₂-CH₂Si(CH₃)Cl₂. (CH3)3SiCl was the principal product obtained, which must be due to the Card 5/7

"APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001859210018-6

	89911
Organosilicon compounds with	S/062/61/000/002/007/01 B115/B207
following intermolecular reaction (9).
$(CH_3)_3$ SiCH ₂ CH ₂ $\xrightarrow{1}$ Si (CH \rightarrow (CH ₃) ₃ SiCl + Al ₂ B	$H_3)_3 \cdot Al_3Br_4 + Cl \xrightarrow{1} SiCl (CH_3) CH_2CH_2Si (CH_3) Cl_3 \rightarrow r_4 + (CH_3)_3 SiCH_2CH_2SiCl (CH_3) CH_2CH_2Si (CH_3) Cl_2 $ (9)
Polycondensation arso proceeds under	
containing the disilethane group and reaction (8)	the -Si-O-Si- group. Thus, in the
[CISI (CH ₃) ₂ CH ₂ CH ₃ Si (CH ₃) ₂] ₂ O + AlCl ₃ -
→ 2GI	Si $(CH_3)_2$ CH_2CH_2Si $(CH_3)_2$ $Cl + [AloCl]$ (8
a considerable amount of a mixture of chlorides forms simultaneously with $(\alpha-\omega$ -dichloride). The polycondense case of other α , ω -hexamethyl disilar	the principal product
•	, , , , , , , , , , , , , , , , , , ,

Organosilicon compounds with ...

S/062/61/000/002/007/012 B115/B207

The compounds with n=1, 3, 4, 5 studied by the authors formed $Si(CH_3)_4$ and a polymeric silicon hydrocarbon consisting of disilalkane fragments also in the reaction with aluminum halides. The authors thank Yu. P. Yegorov and L. A. Leytes for making the spectrum analysis. There are 10 references: 7 Soviet-bloc and 3 non-Soviet-bloc.

ASSOCIATION:

Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED:

September 19, 1959; supplemented June 18, 1960

X

Card 7/7

15.8170

25216

S/062/ 61/000/007/006/009 B117/B215

AUTHORS: Vdovin, V. M., Pushchevaya, K. S., and Petrov, A. D.

TITLE: Organosilicon compounds with hydrocarbon bridges between silicon atoms

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 7, 1961, 1275 - 1279

TEXT: Information 2. Interaction with aluminum halides. The present paper reports on the behavior of 1,3-disilpropane during polycondensation. The disilpropane compounds used were produced by a known method (Ref. 5: V. M. Vdovin i A. D. Petrov, Zh. obshch. khim. 30, 838 (1960)). Their properties are the same as those described in publications (Refs. 5 and 6: A. V. Topchiyev, N. S. Nametkin i S. G. Durgar'yan, Zh. obshch. khim. 30, 927 (1960)). The -[Si(CH₃)₂CH₂CH₂CH₂-]_n - polymer was obtained in the form of a colorless, viscous oil with a boiling point > 300°C by the method of Ref. 3 (V. V. Korshak, A. M. Polyakova i dr. Izv. AN SSSR, Otd. khim. n., 1959, 1116). Chemically pure AlX, preparations were used. The reaction of 1,3-disilpropane compounds with aluminum halides was Card 1/6

2523.6

S/062/61/000/007/006/009 B117/B215

Organosilicon compounds ...

conducted in a flask with descending cooler and a vessel for low-boiling products. $(0 \div -10^{\circ}\text{C})$. Test conditions are tabulated. The reaction follows the scheme

The properties of the substances obtained in both cases proved identical. The examination of the activity of 1,3-disilpropane derivatives with different ratios of CH₂- and Cl groups on the Si atom showed that their activity decreases such:

The last member in the sequence does not react at 200°C in the presence, of AlBr₃ used in amounts up to 40 mole%. According to the low-boiling Card 3/6

s/062/61/000/007/006/009 B117/B215

Organosilicon compounds with .. products, the transformation in the case of (II) and (III) is similar to reaction (b) of Ref. 1. The formation of Si(CH₃)₄ from trichloride (III) indicates that the reaction follows an intramolecular mechanism. the low-boiling products, a polymer residue forms which contains the low-boiling products, a polymer residue forms which contains hydrolyzable chlorine: During reaction (1) at 90 - 100 C, up to 0.95 M Si (CH₃)₄ per mole of (CH₃)₃SiCH₂CH₂CH₂CH₂Si(CH₃)₃ is separated, and a rubber-like polymer with a structure near[-Si(CH3)2CH2CH2CH2-](SiC5H10 The formation of Si(CH3)4 sets in again after further effective heating, and especially in the presence of considerable amounts of catalyst. It was assumed that the developing linear disilpropene . polymers undergo cross-linking in effective heating which follows a scheme similar to (1), where Si...y. CH2CH2CH2Si = bonds are ruptured. and a spatial This reaction is accompanied by a formation of Si(OH3)4 polymer of the type = SiCH2CH2CH2Si-CH2CH2CH2Si=

card 4/6

s/062/61/000/007/006/009 B117/B215

Organosilicon compounds with .

This assumption was proven by heating the linear polymer -[Si(CH3)2CH2CH2CH2 -]n with AlCl3: Si(CH3)4 was separated from the reaction mixture, and an unsoluble, cross-linked polymer formed. 1,3-disilpropane compounds like in 1,2-disilethane derivatives, the temperature of the beginning reaction was lowered by an increase of the molar AlX3 percentage. AlBr3 proved a more active catalyst than AlCl3. The cleavage of Si-C bonds in disilpropane groups apparently also takes place if the compound contains = SiCH2CH2CH2CH2Si = and = Si - 0 - Si = groups. There are 1 table und 9 references: 7 Soviet-bloc and 2 non-Soviet-bloc. The two references to English-language publications read as follows: Ref. 2: I. W. Curru et. al.: J. Organ, Chem. 23, No 8, 1219 (1958); Ref. D. Hurd, J. Amer. Chem. Soc. 67, 1813 (1945).

Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. ASSOCIATION:

Zelinskiy of the Academy of Sciences USSR)

SUBMITTED:

August 26, 1960

Card 5/6

29520 5/062/61/00)/011/007/012

B103/B147

53700

Vdovin, V. M., Sultanov, R., Sladkova, T. A., Freydlin, L. Kh., AUTHORS:

and Petrov, A. D.

Addition of alkoxy silane hydrides to unsaturated nitriles TITLE:

and hydration of the ω -cyano-alkyl-alkoxy silanes produced

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh

nauk, no. 11, 1961, 2007 - 2012

TEXT: The authors studied the addition of alkoxy silane hydrides to: a) allyl cyanide; b) β -cyano-ethyl ether of allyl alcohol; and c) acrylonitrile. It has been found that the addition takes place as follows: $R'(RO)_2SiH + CH_2 = CHCH_2X \longrightarrow R'(RO)_2SiC_2H_4CH_2X$, $R'being -CH_3$, $-OC_2H_5$, or -OCH3; R being -CH3, or -C2H5; and X being -OCH2CH2CN, or -CN. The reaction takes place already at atmospheric pressure, if a mixture of equimolar quantities of the reagents is boiled in the presence of Pt/C (20% of Pt) or a 0.1 N solution of H2PtCl6 in isopropyl alcohol. The yields in addition products were 40 - 50% related to the components used, and up to Card 1/ 4

29520 S/062/61/000/011/007/012 B103/B147

Addition of alkoxy silane hydrides...

85% related to reacted unsaturated nitrile. Yields can be increased and the reaction time essentially reduced in sealed glass ampullas. The main reaction was accompanied in all cases by a disproportionation of the alkoxy radicals of the initial alkoxy silane hydrides: 2(C2H50)3SiH \rightarrow $(c_2H_50)_4Si + [(c_2H_50)_2SiH_2]$, whereby the dihydride formed continued to disproportionate. The frequencies of -CH3 groups were absent in the infrared absorption spectra of the ω -cyano-alkyl trichlorosilane. For this reason, the structures: Cl_3SiCH_2CH_2CH_2CH and Cl_3SiCH_2CH_2CH_2CH_2CN were attributed to these nitriles. The ω -cyano-alkyĺ-trialkoxy silanes which were produced by addition of both trialkoxy silane hydride and HSiCl; to unsaturated nitriles, had identical properties. Thus, it is concluded that the addition of both (RO) SiH and Cl SiH to these nitriles proceeds in the same way, i. e., that the trialkoxy silyl group is placed at the end of the molecule. The interaction of $CH_3(OC_2H_5)_2SiH$ and unsaturated nitriles results perhaps in a mixture of products added to the double bond. This is proved by the wide boiling ranges of these products. An Card 2/

29520 S/062/61/000/011/007/012 B103/B147

Addition of alkoxy silane hydrides...

addition to the triple bond $-C \equiv N$ which could be possibly expected (in analogy to the data of Ref. 7, R. Calas et al. Compt. rend. 252, 420 (1961)), did not occur. Addition of (C2H50)3SiH to acrylonitrile was achieved neither at atmospheric nor at elevated pressure in the presence of catalysts and other substances (in glass ampullas at 150 - 180°C); whereas acrylonitrile was polymerized and triethoxy silane disproportionated, or the initial substances remained unchanged. The ω -cyano-alkyl-triethoxy silanes produced were hydrated to the relevant primary amines in the presence of Co or Ni skeleton catalysts under pressure according to the previously described methods (A. D. Petrov et al. Dokl. AN SSSR, 129, 1064 (1959); L. Kh. Freydlin et al. Izv. AN SSSR, Otd. khim. n. 10, 1878 (1960); V. N. Vdovin et al., author's certificate, SSSR 133683: Byull. izobreteniy SSR 23 (1960)) (Table 2). It has been found that the catalyst type and the structure of the nitrile have a remarkable effect on the yield in in primary amine. The reaction was more selective in the presence of Co catalysts than of Ni catalysts. The yield in amine was higher on hydration of f -cyano-alkyl-trialkoxy silene than on reduction of R-cy: no-ethyl-triethoxy silane. It has been established that hydration of z, \omega -(dicy no-alkyl)-tetracthoxy disilow near to the relevant Card 3/

29520 S/062/61/000/011/007/012 B103/B147

Addition of alkoxy silane hydrides ...

primary \$\psi\$, \$\omega\$ -diamines is possible (Table 3). The \$\psi\$, \$\omega\$ -dinitriles mentioned were formed as by-products of etherification of \$\omega\$-cyano-alkyl-trichlorosilanes. There are 3 tables and 12 references: 5 Soviet and 7 non-Soviet. There most recent references to English-language publications read as The three most recent references to English-language publications read as follows: Ref. 3: L. H. Sommer et al. J. Amer. Chem. Soc. 79, 2764 (1957); Ref. 6: V. B. Jex, J. Mc Mahon, US-Patent 2907784; Chem. Abstr. 54, 4388 (1960); Ref. 11: B. V. Aller, J. Appl. Chem., 7, 130 (1957).

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii

nauk SSSR (Institute of Organic Chemistry imeni N. D.

Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: June 15, 1961

Table 1 Properties of organosilicon nitriles and dinitriles. Legend: (1) boiling point (p, mm Hg); (2) found; (3) calculated.

Table 2. Catalytic hydration of alkyl-cyano silanes in the presence of skeleton catalysts

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S/079/61/031/010/005/010

D227/D303

15.8170

Petrov, A.D., Vdovin, V.M., Golubeva, G., and

Pushchevaya, K.S.

TITLE:

AUTHORS:

Organosilicon compounds with hydrocarbon bridges

between silicon atoms. IV. Pyrolysis of α , ω -

disilalkanes

PERIODICAL:

Zhurnal obshchey khimii v. 31, no. 10, 1961,

3230-3234

TEXT: In the present work the authors studied the pyrolysis of α,ω - disilalkanes of the type $R_3Si(CH_2)_n$ SiR₃ where R is Cl or CH_3 and n = 1 to 4, at $600^{\circ}C$ in a continuous flow system. The thermal stability of these compounds was determined by the quantity of 1) Gaseous and low boiling products; 2) Heavy residues; 3) Gases evolved. The decreasing order of stability of the investigated α , ω - hexamethyldisilalkanes is as follows: K,

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Organosilicon compounds ...

Si(CH₃)₃>(CH₃)₃Si(CH₂)₄Si(CH₃)₃

and the results of pyrolysis are represented in Table 1 where A is the weight % of gaseous and low boiling product and is calcu-

 $\frac{M_1-M_2}{M_1-1}$, M_1 = weight of the original disilalkane, M_2 =

weight of pyrolysis products after distillation of low boiling products, B is the volume of gas (at 20 + 2°C) in ml. per 0.1 g. mol. of disilalkane at a given flow rate; and C is weight % of high boiling residues. Experimental procedure: The pyrolysis was carried out in a quartz tube heated to 600 ± 5°C and the products

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Organosilicon compounds ...

collected in a trap cooled to -10 to -15°C. Fractionation of products was done using a column with 20 theoretical plates and the fractions obtained were analyzed spectrometrically. Compound I gave gaseous products consisting of 93.9% H2 and 6.1% CH4; compound III yielded 13.5% CH₂ = CHSi(CH₃)₃ b.pt 54-55°C, low boiling products mainly $(CH_3)_3$ SiH and $(CH_3)_4$ Si and gases H_2 , CH_4 , C2H6 and C2H4. Compound II decomposed into (CH3)3 SiH and $Si(CH_3)_4$ and also $(CH_3)_3$ SiCH = CH_2 , with H_2 , CH_4 , C_2H_6 , C_2H_4 and C3H6. Compound IV gave a fraction, b.pt 0-53 C, containing (CH₃)₃SiCH₂CH=CH₂ and (CH₃)₃ SiCH₂CH=CH₂; also gaseous products as above. $Cl_3SiCH_2CH_2SiCl_3$ decomposed into $HSiCl_3$, $SiCl_4$ and a mixture of CH₂ = CHSiCl₃ and CH₃CH₂SiCl₃. Compound Cl₂(CH₃)-SiCH2CH2Si(CH3)Cl2 yielded beside CH3SiCl2H and CH3SiCl3 a mixture

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Organosilicon compounds ...

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composed of $CH = CHSi(CH_3)Cl_2$ and $CH_3CH_2Si(CH_3)Cl_2$. The formation of (CH₃)₃SiH during the pyrolysis of II, and Cl₃SiH and CH₂ = CHCH2SiCi3 during the pyrolysis of VII (Cl3SiCH2CH2CH2SiCl3) indicates breaking of the Si-C bond in the disilpropane chain. At the same time, separation of CH₂=CHSi(CH₃)₃ from products of pyrolysis of II, and Cl₃SiCH₃ and CH₂ = CHSiCl₃ from VII is due only to the breaking of C-C bond in the bridging groups. It may be said that under the action of high temperatures Si(CH2)nSi (n>2) decomposes along Si-C as well as C-C bonds. There are 1 figure, 1 table and 16 references: 6 Soviet-bloc and 10 non-Soviet-bloc. The 4 most recent references to English-language publications read as follows: M. Kumada et alia, J. Org. Chem. 23, 252 (1958); K. Shijna, M. Kumada, J. Org. Chem. 23, 139 (1958); A.I. Barry et alia incl. a. End. Chem. 51, 131 (1959); P.D. Genorge et alia Chem. Reve. 56, 1074, 1075, 1077 (1956). orge et alia, Chem. Revs. 56, 1074, 1075, 1077 (1956).

APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001859210018-6"

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27905

S/079/61/031/010/005/010 D227/D303

Organosilicon compounds ...

ASSOCIATION: Institut organicheskoy khimii im. N.D. Selinskogo Akademii nauk SSSR (Institute of Organic Chemistry im. N.D. Selinskiy, Academy of Sciences USSR)

SUBMITTED:

September 30, 1960

Card 5/6

88571

s/020/61/136/001/019/037 B016/B055

5.3700

AUTHORS:

Wdovin, V. M., Pushchevaya, K. S., Belikova, N. A.,

Sultanov, R., Plate, A. F., and Petrov, A. D., Corresponding

Member AS USSR

TITLE:

Derivatives of Silanes With Hydrocarbon Bridges Between the

Si Atoms. The Polymerization of 1,1-Dimethyl Silicocyclo-

pentane

Doklady Akademii nauk SSSR, 1961, Vol. 136, No. 1, pp. 96-99 PERIODICAL:

TEXT: The authors studied the effect of aluminum halides (AlCl3 and AlBr3 on 1,1-dimethyl silicocyclopentane. They regard the latter as a bridge compound in which both ends of the organic radical -R- are attached to the same silicon atom. Experimental results confirmed the authors assumption that, under the influence of AlX3, the \equiv Si - (CH2)4 bonds would be more reactive than the ΞSi - CH_3 bonds. As expected, this lead to formation of a reactive radical -Si(CH3)2CH2CH2CH2CH2-, and in the presence Card 1/3

88571 S/020/61/136/001/019/037 Derivatives of Silanes With Hydrocarbon Bridges B016/B055 Between the Si Atoms. The Polymerization of 1,1-Dimethyl Silicocyclopentane

of AlCl3 or AlBr3 to a specific polymerization reaction (A):

 $(CH_3)_2Si(CH_2)_4 \xrightarrow{Al_2X_6} [(CH_3)_2Si(CH_2)_4] \cdot Al_2X_6 \xrightarrow{(A)_4}$

 $\longrightarrow [-(\text{CH}_3)_2 \text{Si}(\text{CH}_2)_4 -] \cdot \text{Al}_2 \text{X}_6 \longrightarrow -[\text{Si}(\text{CH}_3)_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2] \text{ n } - + \text{Al}_2 \text{X}_6 \text{(A)}$ This reaction is very rapid if the silane and the catalyst are heated for a short time. The authors verified the structure of this product by synthesizing it from corresponding fragments (B). Infrared spectroscopy proved these two products to be identical. Differences between the spectra of these two polymers and that of the monomer are explained by the spacial position of the carbon chains (isomerism). The authors thank Yu. P. Yegorov and Ye. D. Lubush for performing the spectroscopic analyses. Finally the authors discuss the polycondensation of 1,4-ditrimethyl disilyl butane. The reaction product was a colorless, rubbery insoluble polymer similar to the polymerization product obtained in reaction (A). There are 1 figure and 6 Soviet references.

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"APPROVED FOR RELEASE: 08/31/2001 CIA-RDP86-00513R001859210018-6

88571

S/020/61/136/001/019/037 B016/B055 Derivatives of Silanes With Hydrocarbon Bridges Between the Si Atoms. The Polymerization of 1,1-Dimethyl Silicocyclopentane

Institut organicheskoy khimii im. N. D. Zelinskogo Akademii ASSOCIATION:

nauk SSSR (Institute of Organic Chemistry imeni N. D.

Zelinskiy of the Academy of Sciences USSR)

October 1, 1960 SUBMITTED:

Card 3/3

s/020/61/138/004/011/023 B103/B203

15.8170

AUTHORS:

Vdovin, V. M., Sultanov, R., Lubuzh, Ye. D., and Petrov, A. D.,

Corresponding Member AS USSR

Organosilicon compounds with hydrocarbon bridges between the TITLE:

silicon atoms. Alkylation of w-cyano-alkyl trimethyl silanes

by means of halogen methyl trimethyl silanes

Akademiya nauk SSSR. Dcklady, v. 138, no. 4, 1961, 831-834 PERIODICAL:

The authors studied the production of bridge disilanes $(CH_3)_3Si-R-Si(CH_3)_3$ containing a cyano group in the hydrocarbon radical R. Such disilanes may be used for producing various polymers. These compounds $\mathcal J$ have so far been obtained with difficulty. The authors point out that the cyano group bound to the β -carbon atom (with respect to $\hat{S}i)$ can be transformed into various functional groups without separating the cyano-alkyl radical from the Si atom. The reaction was conducted according to the

scheme $(CH_3)_3$ Si $(CH_2)_n$ CH2CH \xrightarrow{Na} $(CH_3)_3$ Si $(CH_2)_n$ CH(Na)CN]

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X

24051 s/020/61/138/004/011/023 n103/8203

Organosilicon compounds with hydrocarbon ...

 $XCH_2Si(CH_3)_3$ (CH₃)₃Si(CH₂)_n $CH_2Si(CH_3)_3 + NaX$, (1) under the conditions

of alkylation of acetonitrile, where n is 1 or 2, and X is Cl, Br, or I. The structure of the compounds obtained was studied by their infrared spectra. The frequency 2238 cm⁻¹ of disilane nitriles lies in a region characteristic of the cyano group, but is a little lower than its value in ω -nitriles (CH₃)₃Si(CH₂)_nCN (for n = 2 and 3, 2249 cm⁻¹). This may well be reconciled with the reduction of the frequency of an electronegative group with increasing branching of the radical bound to this group. Besides, the structure of the compounds produced was confirmed by their transformation into ketones. The highest nitrile yield was obtained according to reaction (1) for (CH₃)₃SiCH₂I (about 40%). In the case of (CH₃)₃SiCH₂Cl, the disilane nitrile yield was lowest (about 20%). In parallel to reaction (1), numerous by-products were formed which corresponded to the dimer of the initial β -cyano-ethyl trimethyl silane. The dimerization of siliconthe

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21051 S/020/61/138/004/011/023 B103/B203

Organosilicon compounds with hydrocarbon, ...

free nitriles under the action of sodium is known, and was confirmed by an additional experiment. From the two structures ascribed to such dimers,

(A) and (B): $RCH_2 - C - CH - R$ $RCH_2 - C - C - H - R$ (A) NH CN

(B) NH₂ CN

the authors choose (B) on the basis of spectral data, where $R=-CH_2Si(CH_3)_3$. Here, they find the frequency 2201 cm⁻¹ (apparatus MKC-12, IKS-12) which they consider to be that of the valency group -CmN. This frequency is reduced, apparently owing to a chain of conjugate groups. The frequencies 3400 and 3448 cm⁻¹ correspond to the symmetric and asymmetric stretching vibrations of the NH₂ group. In the infrared spectrum of the solution of this substance in CCl_4 , the frequency 1630 cm⁻¹ is characteristic of the -C=C bond. The ultraviolet spectrum of this substance showed an intensive frequency 248 mµ (E=46500). In the alkylation of the ω -nitrile of the type $NC-CH_2-CH_2-O-(CH_2)_3Si-(CH_3)_3$, a different reaction occurred:

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Organosilicon compounds with hydrocarbon...

SOFT MALE AND AND AND ADDRESS OF TAXABLE PARTY.

γ-hydroxy-propyl-trimethyl silane and an acrylonitrile polymer were formed. In a control test (without XCH₂Si(CH₃)₃), a γ-alcohol was also formed according to scheme (4) (a = ether, b = polymer). Decomposition of the systems - Y = C - C - C - M(Y - electronegative, M - electropositive atom) was thoroughly studied by A. N. Nesmeyanov and co-workers (Ref. 14: Izbr. tr. (Selected papers), Izd. AN SSSR, 1959. p. 549, 578, 684), and is a characteristic of these systems if M is a metal. In a special experiment, the authors found that the alcoholate (CH₃)₃Si(CH₂)₃ = ONa formed in the reaction did not react with XCH₂Si(CH₃) under given conditions. There are 1 table and 18 references: 10 Soviet-bloc and 8 non-Soviet-bloc. The three references to English-language publications read as follows: Ref. 8: S. Nozakura, S. Konotsune, Bull. Chem. Soc. Japan, 29, No. 3, 322 (1956); ibid., 29, No. 3, 326 (1956); Ref. 10: R. A. Show, J. Chem. Soc., 1956, 2779; Ref. 11: H. Adkins, J. Whitman, J. Am. Chem. Soc., 64, 150 (1942).

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

Card 4/5

30727 3/020/61/141/003/009/021

Polyakova, A. M., Korshak, V. V., Corresponding Member AS USSR

Vdovin, V. M., and Tambovtseva, Ye. S. AUTHORS:

Study of the polymerization of cyanogenous organosilicon TITLE:

compounds

Akademiya nauk SSSR. Doklady, v. 141, no. 3, 1961, 641-644 PERIODICAL:

TEXT: The polymerizability of cyanogenous alkenyl silane derivatives was studied. These compounds were polymerized (a) under pressure (6000 atm) in the presence of the radical initiators (1) azoisobutyrodinitrile, (2) tert-butyl peroxide, or (3) benzoyl peroxide; (b) at normal pressure with Pt/C or H2PtCl6.6H2O as catalysts. It was found that cyano-isopropoxy alkenyl silane derivatives polymerize at comparatively low temperature. Above 120°C these compounds frequently decompose. Only under the conditions of (a) colorless polymers were obtained at 80°C. For the rest, they were yellow to brown. Some of the experiments ended up with explosive polymerization and charring of the products. Most of the products are slightly soluble (Table 1, nos. 1-22). The authors also

Card 1/6

S/020/61/141/003/009/021 B103/B101 Study of the polymerization studied the interaction of tetraalkyl dihydro-disiloxane derivatives with cyanogenous diallyl silane derivatives, obtaining oily products. Such products had also been obtained previously (V. V. Korshak et al., DAN, 128, 960 (1959)) by treating dialkyl diallyl silane derivatives with the same disiloxanes. The conversion of the monomers (Table 1), which proceeded without explosive polymerization or charring, is illustrated as follows (1) $\text{CH}_2 = \text{CH} \left[\text{OC} \left(\text{CH}_3 \right)_2 \text{CN} \right]_3$ Polymerization of the cyanogenous dialkenyl compounds probably also occurs at the double bonds, possibly involving the formation of cyclic structures OC (CH₃)₄ CN (2)

X

S/020/61/141/003/009/021 E103/E101

Study of the polymerization ...

$$R' = R' = CH - CH_{2} - CH_{2} - CH = CH_{3} - CH_{4} - CH_{5} -$$

(1) = or. There are 1 table and 9 references: 7 Soviet and 2 non-Soviet. The two references to English-language publications read as follows: J. C. Williams, R. A. Pike, F. Fekete, Ind. and Eng. Chem., 51, 939 (1959); R. M. Savage, Rubber Age, 84, 975 (1959).

ASSOCIATION:

Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR). Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

Card 3/6 3

32303 s/020/61/141/004/008/019 в103/в101

15.8170

AUTHORS:

Vdovin, V. M., Pushchevaya, K. S., and Petrov, A. D.,

Corresponding Member AS USSR

TITLE: Organosilicon compounds with carbon bridges between the

silicon atoms. Thermal conversions

PERIODICAL: Akademiya nauk SSSR. Doklady. v. 141, no. 4, 1961, 843 -

846

TEXT: The authors continued their studies on the thermal conversion of the $Si(CH_2)_nSi$ group (Petrov, A. D., Vdovin, V.M. at al.ZhOKh, 31, no. 10 (1961)) by investigating the effect of temperatures up to $400^{\circ}C$ on compounds containing a bridge group. They tested substances of the types $(CH_3)_3Si-(CH_2)_n-Si(CH_3)_3$ and $R(CH_3)_3Si-(CH_2)_n$ in sealed glass ampullas. It has been found that the properties of ∞ , ω -hexamethyl disilyl alkanes with n=2, 3, 4 are not modified at 350 - 360°C by heating for three and several hours. This is also true for five and six-membered cyclanes. Card 1/4

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Organosilicon compounds with carbon ...

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Card 2/4

1,1-dimethyl silico-cyclopentane, for instance, is stable at 390°C for 3 hr. On the contrary, four-membered compounds are polymerized: 1-methyl-1chloro-silico-cyclobutane beginning from 170 -180°C and 1,1-dimethyl silico-cyclobutane beginning from 125 - 130°C. Thereby solid elastic substances are formed which are soluble in the initial monomer as well as in benzene and chloroform. The polymers of an elementary composition similar to that of the initial silico-cyclobutanes have the same infrared spectra (NKC-10(IKS-10) apparatus), if they are produced by the reactions [(I)] or [(II)] (1 = or). On the other hand, the spectrum of the polymer from 1,1-dimethyl silico-cyclobutane differs from that of a (B) structure polymer. Therefore the structure (A) was attributed to the former polymer. Control tests have shown that at 180 - 200°C H-Si(CH₃)(R)-CH₂CH=CH₂ is not is completely polypolymerized noticeably, whereas C1(CH3)Si-(CH2)3 merized. Compounds with Si-H bonds are completely absent in the monomer distilled after incomplete polymerization. The different behavior of silico-cyclobutanes as compared to that of five and six-membered silicocyclanes at elevated temperatures may be due to the tension of the four-

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Organosilicon compounds with carbon ...

membered ring. By thermal polymerization of silico-cyclobutanes very high-molecular products are obtained; this is not so, when linear polymers type are produced by other methods. Raman spectra of the CH2CH2CH2Siof the two cyclanes used were taken by means of an NCN-51 (ISP-51) apparatus. They did not show frequencies of the Si-H or C-C bonds. Presumably, the silico-cyclobutane group is characterized by both a very intense line in the range 430 - 450 cm⁻¹ and lines in the ranges 725, 815, 878, 903, 927, and 1125 cm $^{-1}$. In the Raman spectrum of allyl-methyl chloro hydrosilane the Si-bound allyl group is characterized by the frequencies: 407, 940, 995, 1165, 1300, 1392, 1635, 3003, and 3080 cm⁻¹, whereas the line 2175 cm characterizes the ESi-H bond . The polymer C1(CH₃)SiCH₂CH₂CH₂CH₂ In-was obtained by heating CH₂=CHCH₂SiCl(CH₃)H dissolved in isopropanol with a slight admixture of H2PtCl6 up to 80°C. This polymer is a brittle paraffinoid mass with boiling point of 60 - 65°C, Card 3/4

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s/020/61/141/004/008/019 B103/B101

Organosilicon compounds with carbon ...

The yield was about 60%. which is readily soluble in benzene and CCl_{A} . The polymer of 1-methyl-2-chloro-silico-cyclobutane obtained at 230°C is a transparent rubber-like substance which hydrolizes in air, L. A. Leytes is thanked for making the spectrum analyses. There are 13 references: 8 Soviet and 5 non-Soviet, The three most recent references to Englishlanguage publications read as follows: Ref. 5: L. H. Sommer et al., J. Am., Chem. Soc., 79, 3295 (1957); Ref. 6: C. Earborn, Organosilicon Compounds, London, 1960, p. 370; Ref. 10: R. West, J. Am. Chem. Soc., 76, 6012 (1954),

Institut organicheskoy khimii im. N. D. Zelinskogo Akademii ASSOCIATION:

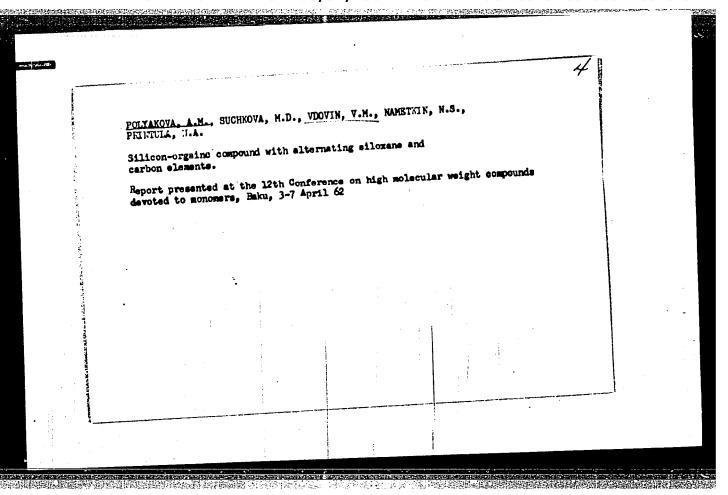
nauk SSSR (Institute of Organic Chemistry imeni N. D.

Zelinskiy, AS USSR)

SUBMITTED:

August 17, 1961

Card 4/4



VDOVIN, V.M.; NAMETKIN, N.S.; PUSHCHEVAYA, K.S.; TOPCHIYEV, A.V.

Expansion reaction of a heterocyclic compound having a silicon atom in its cycle. Izv.AN SSSR. Utd. khim. nauk no.6:1127 '62. (MIRA 15:8)

1. Institut neftekhimicheskogo sinteza AN SSSR. (Silicon organic compounds)

S/074/62/031/007/001/001 1001/1201

AUTHORS:

Vdovin, V. H. and Petrov, A.D.

TITLE:

Silicon-organic compounds containing the (N group

PERIODICAL: Uspekhi khimii, v.31, no.7, 1962, 793-821

TEXT: Review of international and Soviet works on synthesis of CNcontaining silicon-organic compounds: I. Introduction; II. Compounds with a CN group bound directly to silicon atom: 1. Methods of synthesis, 2. Properties. III. Silicon organic compounds with cyanalkyl and cyanaryl radicals: 1. Methods of synthesis; 2. Chemical properties, 3. Physical properties; 4. Use of alkylcyanogen compounds of silicon; IV. Cyanalkosyderivatives of silicon organic compounds: 1. Methods of synthesis, 2. Properties. There are 1 figure, 9 tables and 157 references.

ASSOCIATION:

Institut organicheskoy khimii AN SSSR im N.D. Zelinskogo (Institute of organic chemistry AS USSR,

im. N.D. Zelinskiy)

Card 1/1

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35522
                                                                        s/020/62/143/003/019/029
                                                                        B110/B101
                    Petrov, A. D., Gorresponding Member AS USSR, Vdovin, V. M.,
    11.9200
AUTHORS:
                     and Sultanov, R.
                     Synthesis and conversions of \mathscr{L}_*\omega-di-(alkyl cyanide)
                     tetramethyl disiloxanes
TITLE:
                     Akademiya nauk SSSR. Doklady, v. 165, no. 3, 1962, 606-609
TEXT: The production of &, -di-(alkyl cyanide)-tetramethyl siloxanes
PERIODICAL:
 according to A. D. Petrov et al. (DAN, 128, no. 6 (1959)) was studied.
 The following reactions were carried out:
                                           CH<sub>1</sub>MgH<sub>3</sub>1 H<sub>2</sub>O [XCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SI(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>O +
                                                                                                               (1)
                  XCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>2</sub>)Cl<sub>2</sub> @ эфпр
                                           + XCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SI(CH<sub>3</sub>)<sub>3</sub>,
                                   X = CN, OCH_2CH_2CN Hal = Cl, Br;
                                                                                                                (2)
                            n CH<sub>3</sub>MgHal H_3O [NCCH<sub>2</sub>CH<sub>2</sub>SI (CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>O + NCCH<sub>2</sub>CH<sub>2</sub>SI (CH<sub>3</sub>)<sub>3</sub>,
             NCCHaCHaSiCla
                            Ф афиь
                                                       Hal = Cl, Br, J.
                                      n=2; 2,3; 2,5
  Card 1/4
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S/020/62/143/003/019/029 B110/B101

Synthesis and conversions of ...

(a = ether). During reaction (2) in ethereal medium between -3 and 36° C, optimum yields of α , ∞ -dimitrile were obtained at Hal = Cl and n = 2.5. At n = 2, no large amounts of α , ψ -di-(β -ethyl cyanide) tetramethyl disiloxane were obtained owing to the high rate of substitution at room temperature of all three Cl atoms at silicon from the compound NCCH₂CH₂SiCl₃. Owing to the formation of NCCH₂CH₂Si(CH₃), a considerable part of bifunctional nitrile NCCH2CH2Si(CH3)Cl2 remains in the mixture. This reacts, during the hydrolysis, with the monofunctional NCCH2CH2Si(CH3)2Cl and forms linear polysiloxanes with the presumable structure NCCH2CH2Si(CH3)20 NCCH2CH2(CH3)SiO kSi(CH3)2CH2CH2CN. first link of this series with k = 1 was separated in all experiments. The &, w-di-(alkyl cyanide)-tetramethyl disiloxanes obtained were copolymerized with dimethyl silicon cyclopolysiloxanes at 20 ± 2°C by means of 2-6% by weight of concentrated H2SO4. According to M. Prober (see below), cyclic polysiloxanes with lpha-alkyl cyanide radicals separate the cyanide radical under the given conditions and form crosslinked polymers. The linear of, w-di-(alkyl cyanide) dimethyl polysiloxanes Card 2/4

S/020/62/143/003/019/029 B110/B101

Synthesis and conversions of ...

produced were highly viscous liquids. Their viscosity index was close to that of dimethyl polysiloxanes. In a similar way, disiloxanes with reactive CN-alkyl- and Cl-alkyl groups were obtained:

 $[NC (CH₃)₂Si(CH₃)₂]₂O + n [CICH₂Si(CH₃)₃]₂O \xrightarrow{H_1SO_4}$ $\rightarrow 2NC (CH₃)₂Si (CH₃)₂OSi (CH₃)₃CH₂Cl + (n-1) [CICH₂Si(CH₃)₃]₃O.$ (4)

At n = 7 chloro nitriles with 70-90% yield were obtained. According to:

 $\text{NCCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2 \text{ OSi}(\text{CH}_3)_2\text{CH}_2\text{Cl} \xrightarrow{\text{KI}} \text{NCCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{I},$

the iodide was produced with 83% yield. There are 2 tables. The most important English-language reference is: M. Prober, J. Am. Chem. Soc., 77, 3224 (1955).

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

Card 3/4

Synthesis and conversions: of...

SUBMITTED: December 11, 1961

Gard 4/4

VDOVIN, V.M., ZAVYALOV, V.L., PUSHCHEVAYA, K.S.; NAMETKIN, N. S.;

"Unwardiungen von silicium kohlenstoff heterozyklen mit Si im ring unter einwirkung von AlCl3."
"Conversion of Si-C heterocycles containing Si in the ring under the influence of AICI3."

Report submitted to the 2nd Dresden Symp. on Organic and Non-Silicate Silicon Chemistyy.

Dresden, East Germany 26-30 March 1963

NAMETKIN, N.S., FINKELSHTEYN, Y. 54. VDOVIN, V.M.

"Die alkykierung aromatischer verbindungen mit silico-olefinen."

Report submitted to the 2nd Dresden Symp. On Organic and Non-Silicate Silicon Chemistry.

Dresden, East Germany 26-30 March 1963

NAMETKIN, N.S., VDCVIN, V.M.

Procede nouveau pour la preparation des polymeres silaniques constitues par des atomes de carbone et de silicium dans les chaines principles.

Report submitted at the International Symposium of Macromolecular Chemistry Paris, 1-6 July 63

\$/062/63/000/002**/010/020** B144/B106

AUTHORS: Vdovin, V. R., Nametkin, N. S., Poshchevnya, K. S., and Topchiyev, A. V. (Deceased)

TITLE: Synthesis and conversions of 1-chloro-mathyl-1-methyl silicocyclopentane

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 2, 1963, 274 - 281

TEXT: 1-chloro-methyl-1-methyl silico-cyclopentume (I) (b.p. 168.3°C, n20 1.4738, 14 0.9893) was synthesized from chloro-methyl-methyl-dichloro silane and BrMg(CH₂)₄MgBr in 50% yield. It was used as the initial substance for the synthesis of new derivatives with carbefunctional radicale. The structure of I determined from IR spectra was CH₂-CH₂ Si CH₃. Derivatives were obtained by introducing functional curve of CH₂-CH₂ Si CH₂Cl. Derivatives were obtained by introducing functional groups into the methyl radical by nucleophilic substitution of Cl. 1-iedo-methyl-1-methyl silico-cyclopentane was synthesized from I, KI and acetone

Card 1/3

8/069/63/000/002/010/020 B144/B186

Synthesis and conversions of ...

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2/062/63/000/002/010/026 B144/B186

presence of the Si-Cl bond. The widening of an Si-containing heterogeneous ring has been achieved for the first time. Under the effect of R2DO4 the ring of I was opened and a disiloxane formed.

ASSOCIATION: Institut neftekhimicheskogo sintess Akademii nauk ESBR (Institute of Petrochemical Synthesis of the Academy of Sciences USSR)

SUBMITTED: May 17, 1962

Card 3/3

EPF(c)/EWP(j)/EWT(m)/BDS--AFFTC/ASD--Pr-h/Pc-4--RM/MAY/WW L 11226-63 \$/0062/63/000/005/0822/0831 ACCESSION NR: AP3000123 AUTHOR: Yegorov, Yu. P.; Pushchevaya, K. S.; Lubuzh, Ye. D.; Vdovin, V. M.; Petrov, A. D. TITLE: Organosilicon compounds with hydrocarbon bridges between the silicon atoms SOURCE: AN SSSR. Izvestiya otdeleniye khimicheskikh nauk, no. 6, 1963, 822-831 TOPIC TAGS: organosilicon compounds, polycondensation, polymerization, polymer, structure, IR spectroscopy, aluminum chloride, aluminum bromide ABSTRACT: The feasibility of synthesizing polymers having alternating p-xylylene or p-phenylene radicals and silicon atoms in the backbone by the polycondensation of 1,4-bis(trimethylsilyl)xylylene or 1,4-bis(trimethylsilyl)phenylene in the presence of an Al₂Cl₆ or Al₂Br₆ catalyst has been established. The structure of previously prepared products of the catalytic polycondensation of various a, w-bis(trimethylsilyl)alkanes as well as of the thermal polymerization of 1,1-dimethylsilacyclopropane and 1,1-dimethylsilacyclobutane have been studied by IR spectroscopy. The structure of the polymer of 1,1-dimethylsilacyclopentane,

THE RESERVE OF THE PROPERTY OF

NAMETKIN, N.S.; VDOVIN, V.M.; PUSHCHEVAYA, K.S.

Catalytic reactions involved in the formation of 1,1-dimethyl-silicocyclopentane. Dokl. AN SSSR 130 no.3:562-565 My '63.

(MIRA 16:6)

1. Institut neftekhimicheskogo sinteza AN SSSR. 2. Chlenkorrespondent AN SSSR (for Nametkin). (Silicon organic compounds) (Catalysis)

L 13007-63

EPF(c)/EWP(j)/EWT(m)/BDS

AFFTC/ASD

Pc-4/Pr-4

RM/WW/MAY

ACCESSION NR: AP3001403

5/0020/63/150/004/0799/0801

56

AUTHOR: Vdovin, V. M.; Nametkin, N. S. (Corresponding Member of Academy of Sciences, SSSR); Grinberg, P. L.

TITLE: Cyclobutanesilicates. The synthesis of 1,1-substituted cyclobutanesili-

SOURCE: AN SSSR. Doklady, v. 150, no. 4, 1963, 799-801

TOPIC TAGS: Synthesis of 1-chlor-1-methylcyclobutanesilicate, synthesis of 1-methyl-1-benzylcyclobutanesilicate, 1-ethyl-1-methylcyclobutanesilicate

ABSTRACT: The study of metaloorganic reactions of Y -chloropropyl silicate derivatives of the type

Cl₂RSiCH₂CH₂CH₂Cl \xrightarrow{M} CIRSi (CH₂)₃ $\xrightarrow{}$ R = CH₃; Cl; M = Na; Li; Mg

showed that the reaction with the non-activated magnesium in ether resulted in very low yields of cyclobutylsilicates (10%). However, good yields of cyclobutylsilicates were obtained when using magnesium activated with iodine vapors. Further Card 1/2

L 13007-63

ACCESSION NR: AP3001403

preparations of cyclobutylsilicates were made using alkyl, aryl, alkenyl and alkylaryl substitutions on the silica:

 $Cl (CH_2) \underbrace{Si (CH_2)_3}_{\text{ester}} \underbrace{R' MgX}_{\text{ester}} R' (CH_3) \underbrace{Si (CH_2)_3}_{\text{i}}$ $R' = CH_3; C_2H_5; \kappa \cdot C_4H_9; -CH_2CH = CH_2; -CH_2 - \underbrace{CH_2}_{\text{i}}; X = Cl, B_F, J$

The synthesis of 1-chlor-1-methyl-cyclobutanesilicate, 1-methyl-1-bensylcyclobutanesilicate, and 1-ethyl-1-methylcyclobutanesilicate was obtained from hydrosilanes and alyl chlorides with the use of H₂PtCl₆catalyst. Orig. art. has: 2 tables.

ASSOCIFION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute of Petrochemical Synthesis, Academy of Sciences, SSSR)

SUBMITTED: 12Feb63

DATE ACQ: 01Jul63

ENCL: 00

SUB CODE: 00

NO REF SOV: 008

OTHER: 006

Card 2/2

L 22662-65 EPF(c)/EWP(j)/EWT(m)/T Pc--i/Pr-4 RM/MLK ACCESSION NR: AT5002115 S/0000/64/000/000/0091/0006

AUTHOR: Polyakova, A.M.; Suchkova, M.D.; Vdovin, V.M.

TITLE: Synthesis of organosilicon compounds with alternating siloxane (or silane) and carbon members

SOURCE: AN SSSR. Institut neftekhimicheskogo sinteza. Sintez i svoystva monomerov (The synthesis and properties of monomeror Moscow Tzd-vo Nauka, 1964, 91-96

TOPIC TAGS: silicoorganic compound siloxane polymer, silane polymer, oligomer synthesis

ABSTRACT: A general method is proposed for the synthesis of organosilicon oligomers, the main chain of which concerts of alternature hydrocachon and siloxane fragments. The method involves the reaction of K. Widniydroponys. The same dihydrositaness with acetyplene and non-conjugated dioletins in the presence of position catalysts. The structure of the oligomers was demonstrated with the act of infrared absorption spectra, using the absorption bands of the valence oscillations of terminal H-Si (2100-2150 cm⁻¹) and C = C (1595-1600 cm⁻¹) bonds. In order to evaluate the structures containing terminal vinylegroups, use was also made of absorption bands of the asymmetric valence oscillations of

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L 22662-65

ACCESSION NR: AT5002115

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the terminal -CH₂- groups (3050 cm⁻¹). The presence of -CH=CH₂- and H-Si- groups in the molecules of the oligomers was also demonstrated chemically. Reactions on the terminal groups of the resulting oligomers (Si-H and Si-alkene) and functional groups contained in the hydrocarbon chain (=N-H) resulted in solidification of the oligomers into trimeric products. Orig. art. has: 3 tables and 5 formulas.

ASSOCIATION: None

SUBMITTED: 30Jul64

ENCL: 90

SUB CODE: OC, 60

NO REF SOV: 004

OTHER: 001

Card 2/2

L -0851- 1 8-715 0571: 847 0 577	
AUTHOR: Sultanov, R., Vdovin, V. M.	
TITLE: Cyano-containing silico-organic compactifs	
SOURCE: AN SSSR. Institut neffek'unitedeskort stricta. Statez i svoy. (The synthesis and properties of monomers). Moscow, Izd-vo Nauka, 1	stva monomerov 964, 130-154
The PITCH Control of the Control of	ta, kwanoo lefun
ABSTRACT: Pt/C catalysts with 5 or 20% Pt and a 6.1 N solution of H2 alone is very use for the matter of the state of the containing olefins (a) and derivatives of state in-containing and these terms of 1-hydro-1-methylsilicocyclopenture with many containing olefins (c)	that in the reaction
Ripiscal Fig. P. CHCH Finch Chick - Plansch Finger Wellich Chick Chich	-CII,(I) (1)
	EV (
	O C William
Card 1/3	

